A New Reaction of Nitrosyl Complexes; One-electron Reduction of *trans*-[$MX(NO)L_4]^{2+}$ [M = Ru or Fe, X = Cl or Br, L = Pyridine or *o*-Phenylenebis(dimethylarsine)] with Hydroxylamine

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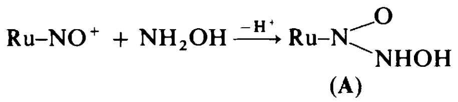
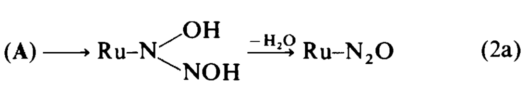
The complexes *trans*-$[MX(NO)L_4]^{2+}$ [M = Ru or Fe, X = Cl or Br, L = pyridine or *o*-phenylenebis(dimethylarsine)] react with hydroxylamine to afford the corresponding one-electron reduced species. The reaction appears to be the first to produce a $(M\text{-}NO)^{2+}$ group.

Recent investigations of the nitrosyl ligand (NO^+) co-ordinated to transition metals have revealed a variety of interesting reactions.[1] The reaction between nitrosyl and hydroxylamine to give dinitrogen monoxide as ligand is one such reaction.[2] According to the proposed mechanism [1c,2] the reaction involves an intermediate (**A**) formed by nucleophilic attack of the hydroxylamine on the nitrosyl nitrogen [equation (1)]. This intermediate is then rearranged and converted into a complex containing a dinitrogen monoxide ligand [equation (2a)]. However, another possible reaction [equation (2b)], which would give a one-electron reduced species, probably *via* the intermediate (**A**), is possible because (*i*) hydroxylamine can serve as a reducing agent and (*ii*) the reactivity of the co-ordinating nitrosyl toward nucleophiles is not always the same for the $[MX(NO)L_4]^{2+}$ type of complex, as has been observed in the reaction with azide.[3–5]

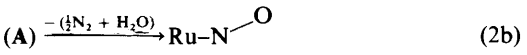


$$Ru\text{-}NO^+ + NH_2OH \xrightarrow{-H^+} Ru\text{-}N\begin{matrix}O\\NHOH\end{matrix} \quad (1)$$

(**A**)



$$(A) \longrightarrow Ru\text{-}N\begin{matrix}OH\\NOH\end{matrix} \xrightarrow{-H_2O} Ru\text{-}N_2O \quad (2a)$$



$$(A) \xrightarrow{-(\frac{1}{2}N_2 + H_2O)} Ru\text{-}N^{\,O} \quad (2b)$$

We report here that the one-electron reduction occurs for both *trans*-$[RuX(NO)(py)_4]^{2+}$ (X = Cl or Br, py = pyridine) and *trans*-$[FeCl(NO)(pdma)_2]^{2+}$ [pdma = *o*-phenylenebis(dimethylarsine)], of the $\{MNO\}^6$ type of complex,† under moderate conditions. No evidence for the formation of a dinitrogen monoxide ligand could be obtained. The reaction appears to be the first to give the six-co-ordinated $\{MNO\}^7$ type of nitrosyl complex,[6] instead of a complex with dinitrogen monoxide as ligand. The reaction is also valuable as a synthetic route to the six-co-ordinated $\{MNO\}^7$ type of complex, of which very few examples have been isolated.[8,9]

The reactions between *trans*-$[MX(NO)L_4]^{2+}$ and hydroxylamine were carried out in the dark, as described later. Product identity was established by comparing properties with those of known similar complexes (Table).[8,9] All $\{MNO\}^7$ type complexes, products (**1**)—(**3**), and the known complexes, (**4**) and (**5**), exhibited a characteristic ν(NO) absorption band near 1 600 cm^{-1}, while the corresponding absorption band due to co-ordinated NO^+ near 1 900 cm^{-1} disappeared. The drastic shift in the ν(NO) absorption bands to lower frequency can be interpreted in terms of a reduction in the nitric oxide bond order upon addition of a single electron to the lowest unoccupied π*(NO) orbital.[9] The effective magnetic moment was comparable to the value expected for the one-electron reduction of the original diamagnetic complexes.

The electrochemical properties of complex (**1**) were studied by d.c. polarography and cyclic voltammetry using a hanging mercury electrode. The original nitrosyl complex, (**6**), $\{RuNO\}^6$, in acetonitrile solution underwent an electrochemically reversible one-electron reduction (first wave) at 0.25 V and an irreversible one-electron reduction (second wave) at −0.58 V, whereas (**1**) showed a one-electron oxidation and reduction waves with $E_{\frac{1}{2}}$ corresponding to the potentials of the first and second waves of (**6**), respectively. Similar observations were made for the redox system $[Fe(CN)_5(NO)]^{2-}$–$[Fe(CN)_5(NO)]^{3-}$;[10] this supports the identification of (**1**) as a $\{RuNO\}^7$ type of complex.

Experimental

Microanalyses were by the Sophia University microanalytical service. Infrared spectra were obtained for KBr discs. D.c. polarographic and cyclic voltammetric experiments were performed in CH_3CN solution using a hanging mercury electrode with tetraethylammonium perchlorate as supporting electrolyte. The measurements were made *vs.* a saturated potassium chloride calomel electrode (s.c.e.) at 25 °C.

The nitrosyl complexes *trans*-$[RuX(NO)(py)_4][ClO_4]_2$ (X = Cl or Br) were prepared as described previously.[5] The salt *trans*-$[FeCl(NO)(pdma)_2][ClO_4]_2$ was prepared by the literature method.[11]

Isolation of Chloronitrosyltetrakis(pyridine)ruthenium Hexafluorophosphate Monohydrate, $[RuCl(NO)(py)_4]PF_6{\cdot}H_2O$ (**1**).—A deaerated aqueous solution of *trans*-$[RuCl(NO)(py)_4][ClO_4]_2$ (100 mg, 0.16 mol) was cooled in ice to 7 °C. To this solution was added an aqueous solution (2 cm^3) of $NH_2OH{\cdot}HCl$ (40 mg) (which had been adjusted to pH 6.5 by $NaHCO_3$). The mixed solution was kept at 7 °C for 1—2 min, and then NH_4PF_6 (30 mg) was added. The pale green precipitate which was obtained was filtered off, washed with water, and then air-dried. Yield 40% (Found: C, 37.6; H, 3.3; Cl, 5.8; N, 11.0. Calc. for $C_{20}H_{22}ClN_5O_2Ru$: C, 37.7; H, 3.3; Cl, 5.7; N, 11.1%).

Analogous products $[RuBr(NO)(py)_4]PF_6{\cdot}H_2O$ (**2**) and $[FeCl(NO)(pdma)_2]PF_6$ (**3**), were obtained using the same procedure from the corresponding $\{MNO\}^6$ complexes {Found: C, 34.6; H, 3.1; N, 9.9. Calc. for $[RuBr(NO)(py)_4]$-

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† Nitrosyl complexes with formal oxidation states of $(Ru^{II}\text{-}NO^+)^{3+}$ and $(Ru^{II}\text{-}NO)^{2+}$ are abbreviated as $\{RuNO\}^6$ and $\{RuNO\}^7$ using the nomenclature proposed by Enemark and Feltham.[6] The formal oxidation state of $(Ru^{II}\text{-}NO^+)^{3+}$ in *trans*-$[RuCl(NO)(py)_4]^{2+}$ could be deduced from the linear structure of the mean RuNO moiety [174.8(9)°].[7]

Table. Properties of the reaction products and related complexes

			$E_{\frac{1}{2}}{}^{b}$/V		
Complex	$\tilde{\nu}(NO)^{a}/cm^{-1}$	$\mu_{eff.}$/B.M.	ox.	red.	Ref.
(**1**) $[RuCl(NO)(py)_4]PF_6$	1 617(1 582)	2.29	0.25	−0.58	*c*
(**2**) $[RuBr(NO)(py)_4]PF_6$	1 610	2.30			*c*
(**3**) $[FeCl(NO)(pdma)_2]PF_6$	1 622				*c*
(**4**) $[RuCl(NO)(bipy)_2]I^{d}$	1 640(1 611)				9
(**5**) $[FeCl(NO)(pdma)_2]ClO_4$	1 625	1.80			8
(**6**) $[RuCl(NO)(py)_4][ClO_4]_2$	1 908(1 877)	*e*		0.25, −0.58	5
(**7**) $[RuCl(NO)(bipy)_2][PF_6]_2{}^{d}$	1 940(1 925)	*e*		0.20, −0.60	9
(**8**) $[FeCl(NO)(pdma)_2][ClO_4]_2$	1 865	*e*			8

[a] As KBr pellets. The figures in parentheses refer to $\nu(^{15}NO)$. [b] *vs.* s.c.e. D.c. polarograms were taken in 0.1 mol dm^{-3} tetraethylammonium perchlorate–acetonitrile solution (25 °C). [c] This work. [d] bipy = 2,2′-Bipyridyl. [e] Diamagnetic.

$PF_6{\cdot}H_2O$: C, 34.8; H, 3.2; N, 10.1. Found: C, 28.9; H, 3.9; N, 1.7. Calc. for $[FeCl(NO)(pdma)_2]PF_6$: C, 28.7; H, 3.8; N, 1.7%}.

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